Nitride Fuel Fabrication Efforts at Los Alamos for the Advanced Fuel Cycle Initiative

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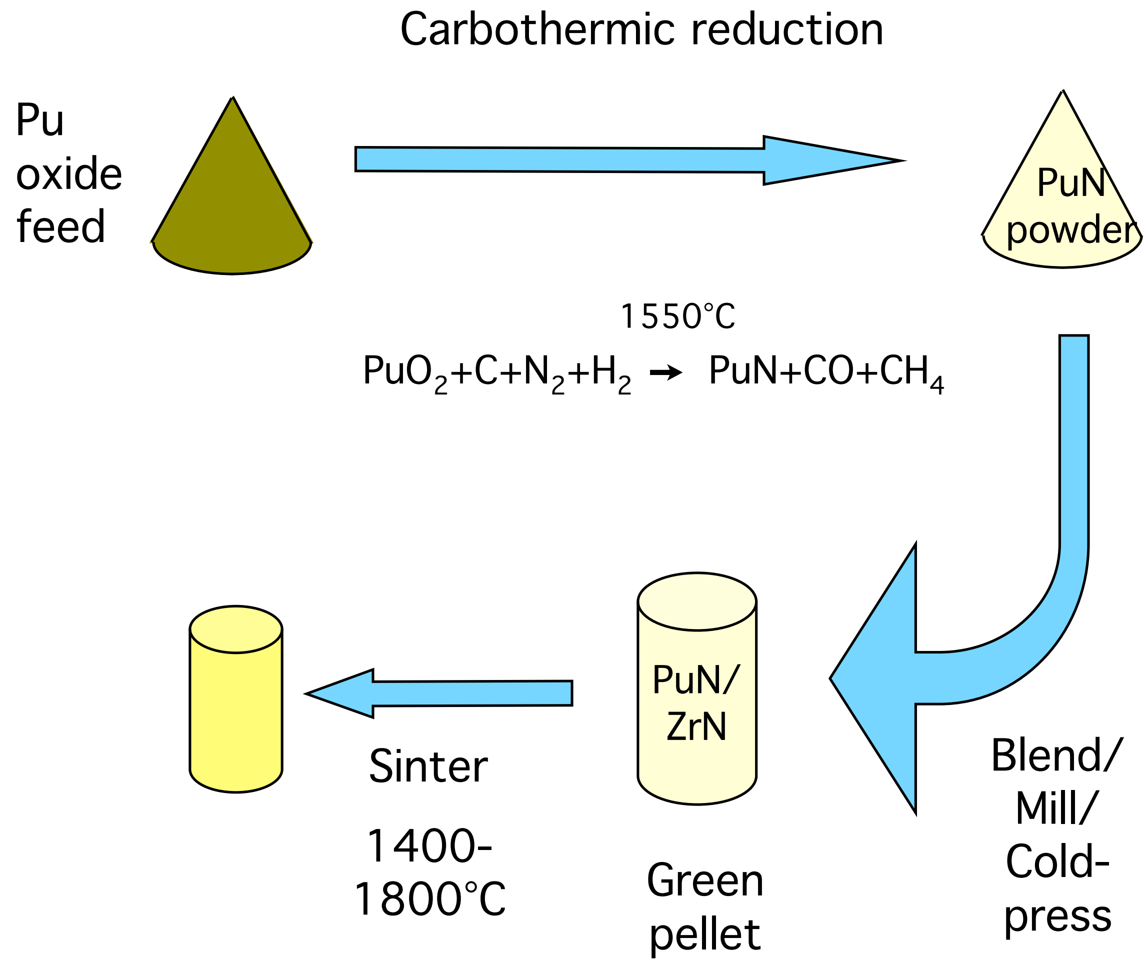
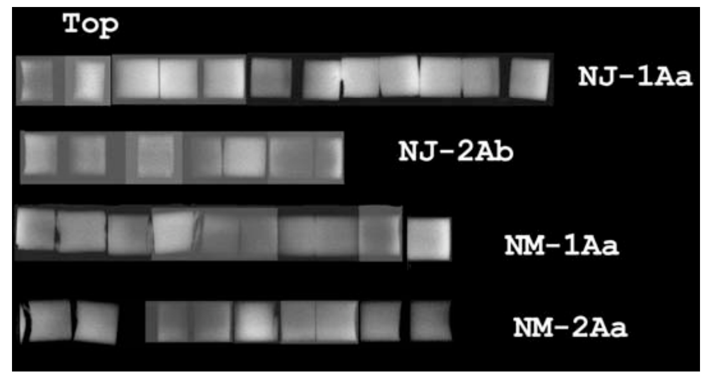
Arizona State U.:	Pedro Peralta
Imperial College:	Robin W. Grimes and Kurt J. W. Atkinson

Pellet cracking persisted

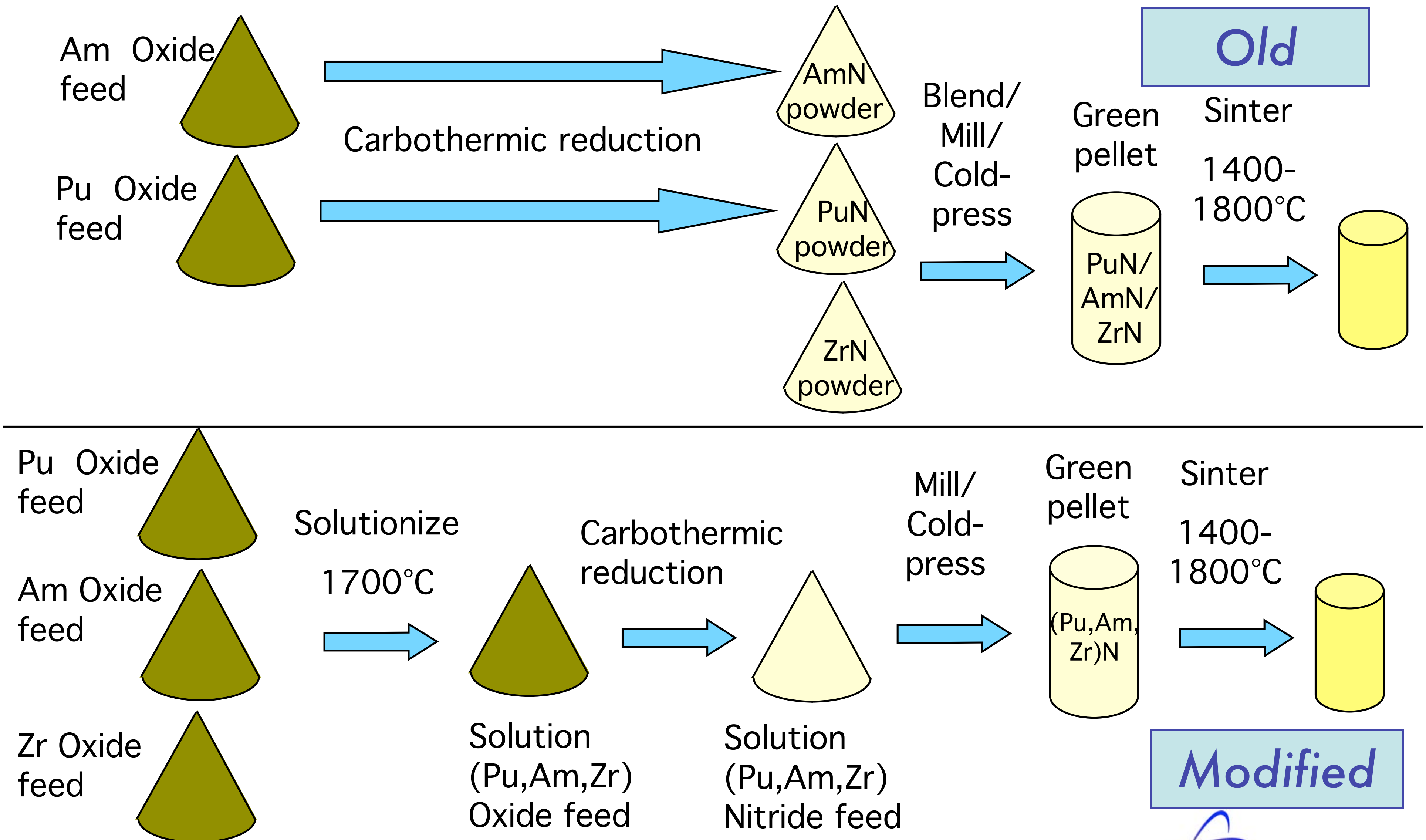


Radiography (ANL)



Alternate synthesis route was necessary

Modified nitride pellet synthesis

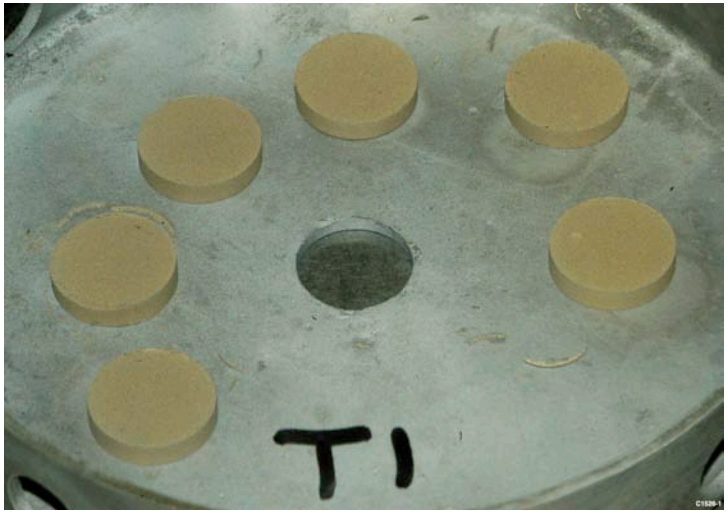


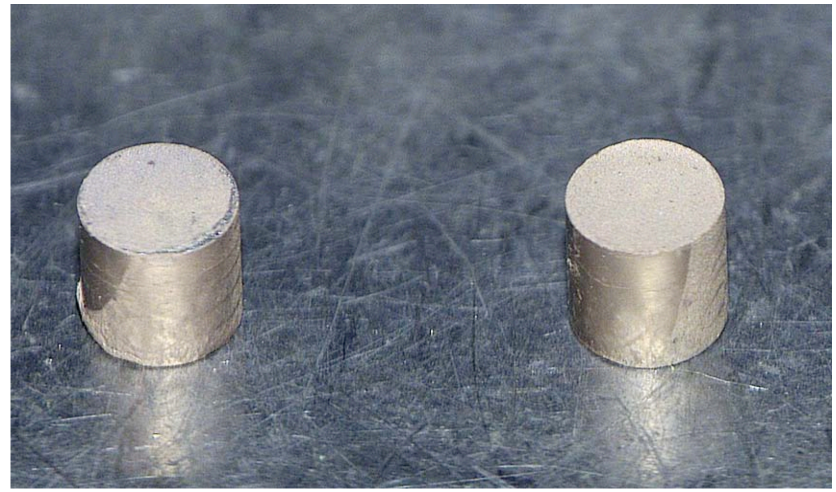
Modified nitride ATR experiment

- Original
  - Wide range of compositions, scientific curiosities, FUTURIX (Phenix) experiment support
  - 6 non-fertile nitride compositions
  - 6 low-fertile nitride compositions
- Modified
  - Focus on FUTURIX experiment support only
  - 3 non-fertile nitride compositions
  - 3 low-fertile nitride compositions

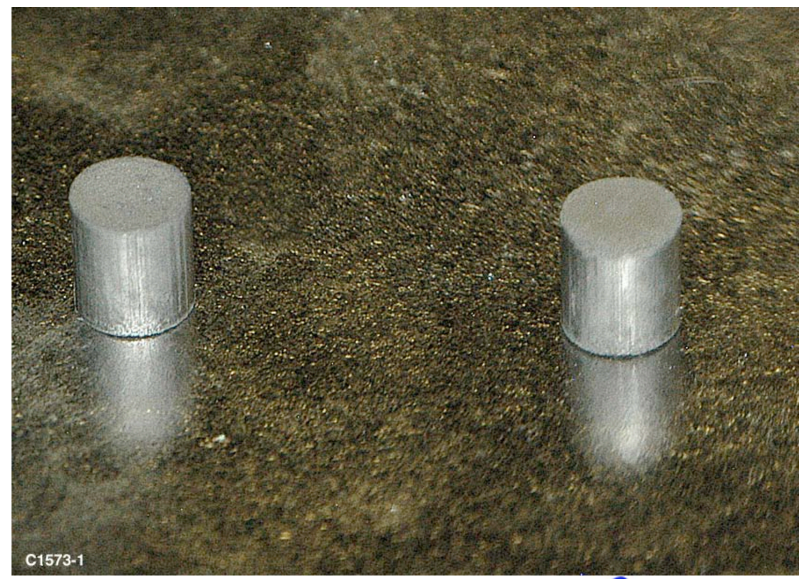
Non- and low-fertile nitrides

Non-fertile (Zr-containing)





Low-fertile (U-containing)



Converted nitride briquettes

Sintered pellets

Non-fertile: pellet fabrication

Sintering: 1600°C/10 hr/argon

FUTURIX Comp	Composition	ATR burn-up position	Average density (SD) (%)	Average wt (SD) (g) green = 0.535 g	Average vol change (SD) (%)	Approx. wt. Loss (%)
Primary	$(Pu_{0.5},Am_{0.5})N$-36ZrN	High	83.6(1.1)	0.512 (0.005)	~20	5.5
Primary	$(Pu_{0.5},Am_{0.5})N$-36ZrN	Low	88.4(1.4)	0.502 (0.006)	~24	6.5
Secondary	$(Pu_{0.5},Am_{0.25}Np_{0.25})N$-36ZrN	Med.	77.7(1.6)	0.518 (0.011)	13.5(1.4)	2.3

Low-fertile nitrides: pellet fabrication

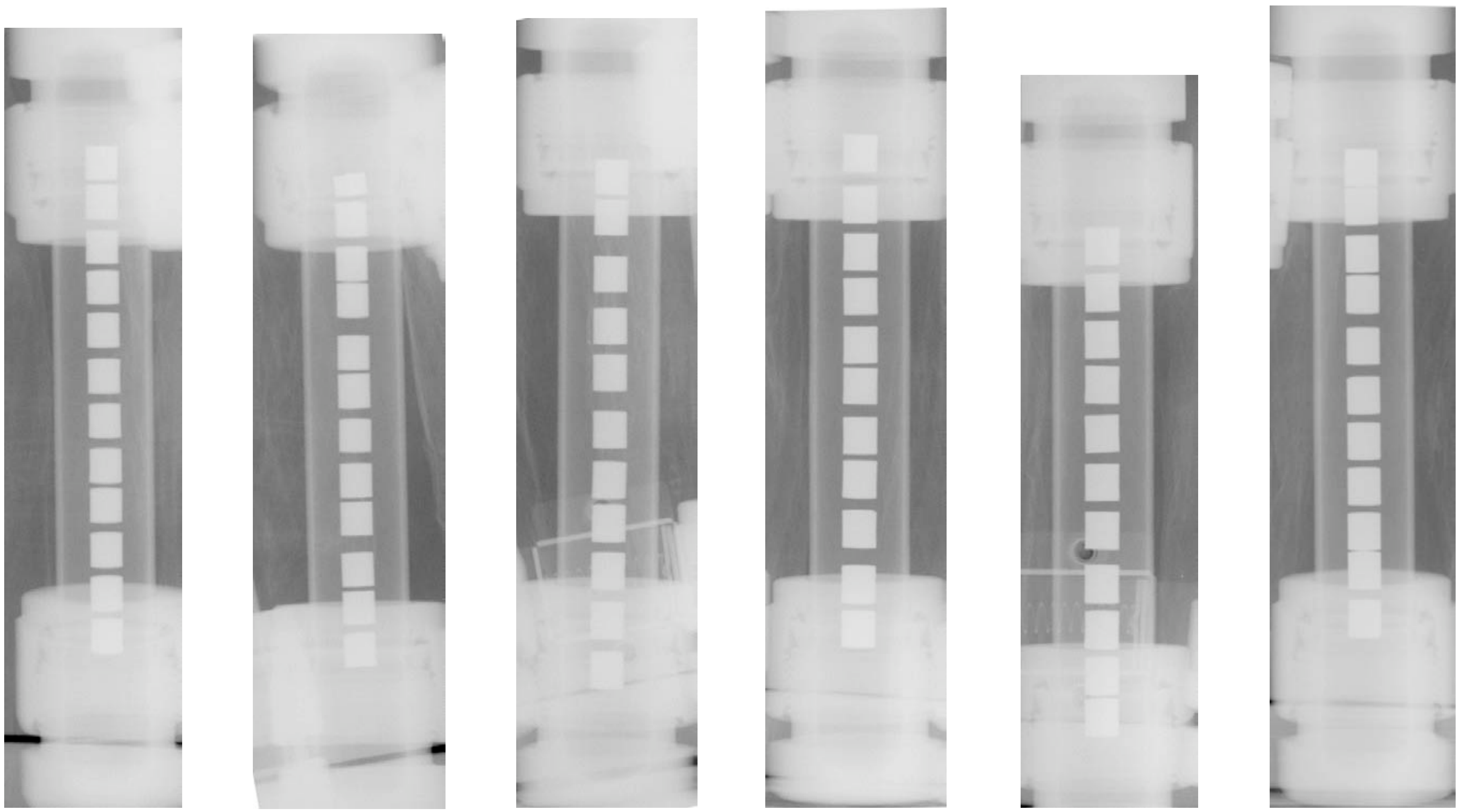
FUTURIX Comp	Composition	ATR Burn-up position	Average Denisty (% TD) Avg(SD)	Approx. wt. Loss (%)
Primary	$(U_{0.5},Pu_{0.25},Am_{0.15},Np_{0.10})N$	High	77.2 (0.8)	1.5
Primary	$(U_{0.5},Pu_{0.25},Am_{0.15},Np_{0.10})N$	Low	77.2 (0.8)	1.5
Secondary	$(U_{0.5},Pu_{0.25},Am_{0.25})N$	Medium	82.4 (1.2)	2.0

Chemical Analysis for AFC1-AE

	Comp11-H		Comp11-L		Comp13		Comp21-H, -L		Comp23	
LIMS no.		2001154123		2001154124		2001154122		2001154649		2001154650
Element	Spec.	Measured	Spec.	Measured	Spec.	Measured	Spec.	Measured	Spec.	Measured
Total Pu (wt.%)	30.0 (±5)	31.8	30.0 (±5)	33.1	30.0 (±5)	31.7	23.6 (±5)	24.8	23.6 (±5)	24.2
Total U (wt.%)	0.0	0.0	0.0	0.0	0.0	0.0	47.2 (±5)	48.6	47.2 (±5)	48.0
Am (wt.%)	30.0 (±10)	26.0	30.0 (±10)	23.0	15.0 (±10)	12.6	14.2 (±10)	12.0	23.6 (±10)	21.0
Np (wt.%)	<1.0	***1.1***	<1.0	***1.3***	15.0 (±5)	12.2	9.44 (±5)	8.0	<1.0	0.8
Zr (wt.%)	31.7 (±5)	33.5	31.7 (±5)	34.3	31.7 (±5)	33.1	0.0	0.2	0.0	0.9
N (wt.%)	n.s.	5.2	n.s.	5.0	n.s.	5.7	n.s.	4.3	n.s.	3.7
O (wt.%)	n.s.	0.8	n.s.	0.7	n.s.	0.8	n.s.	0.4	n.s.	0.6
C (wt.%)	n.s.	1.5	n.s.	1.6	n.s.	1.3	n.s.	0.3	n.s.	0.5
Pu-238 (wt.% of Tot Pu)	<0.10	0.01	<0.10	0.01	<0.10	0.010	<0.10	0.01	<0.10	0.01
Pu-239 (wt.% of Tot Pu)	93.8 (±1)	93.9	93.8 (±1)	93.9	93.8 (±1)	93.90	93.8 (±1)	93.9	93.8 (±1)	93.8
Pu-240 (wt.% of Tot Pu)	n.s.	5.97	n.s.	5.97	n.s.	5.96	n.s.	6.02	n.s.	6.03
Pu-241+ Pu-242 (wt.% of Tot Pu)	<0.50	0.13	<0.50	0.13	<0.50	0.13	<0.50	0.107	<0.50	0.115
U-235 (wt.% of Tot U)	<1.0	0.0	<1.0	0.0	<1.0	0.0	45 (±1)	45	45 (±1)	45
U-238 (wt.% of Tot U)	<1.0	0.0	<1.0	0.0	<1.0	0.0	55 (±1)	54	55 (±1)	54
Impurities	<0.5	0.41	<0.5	0.44	<0.5	***0.77***	<0.5	0.41	<0.5	0.07

n.s.—not specified

Radiography on non- and low-fertile nitrides



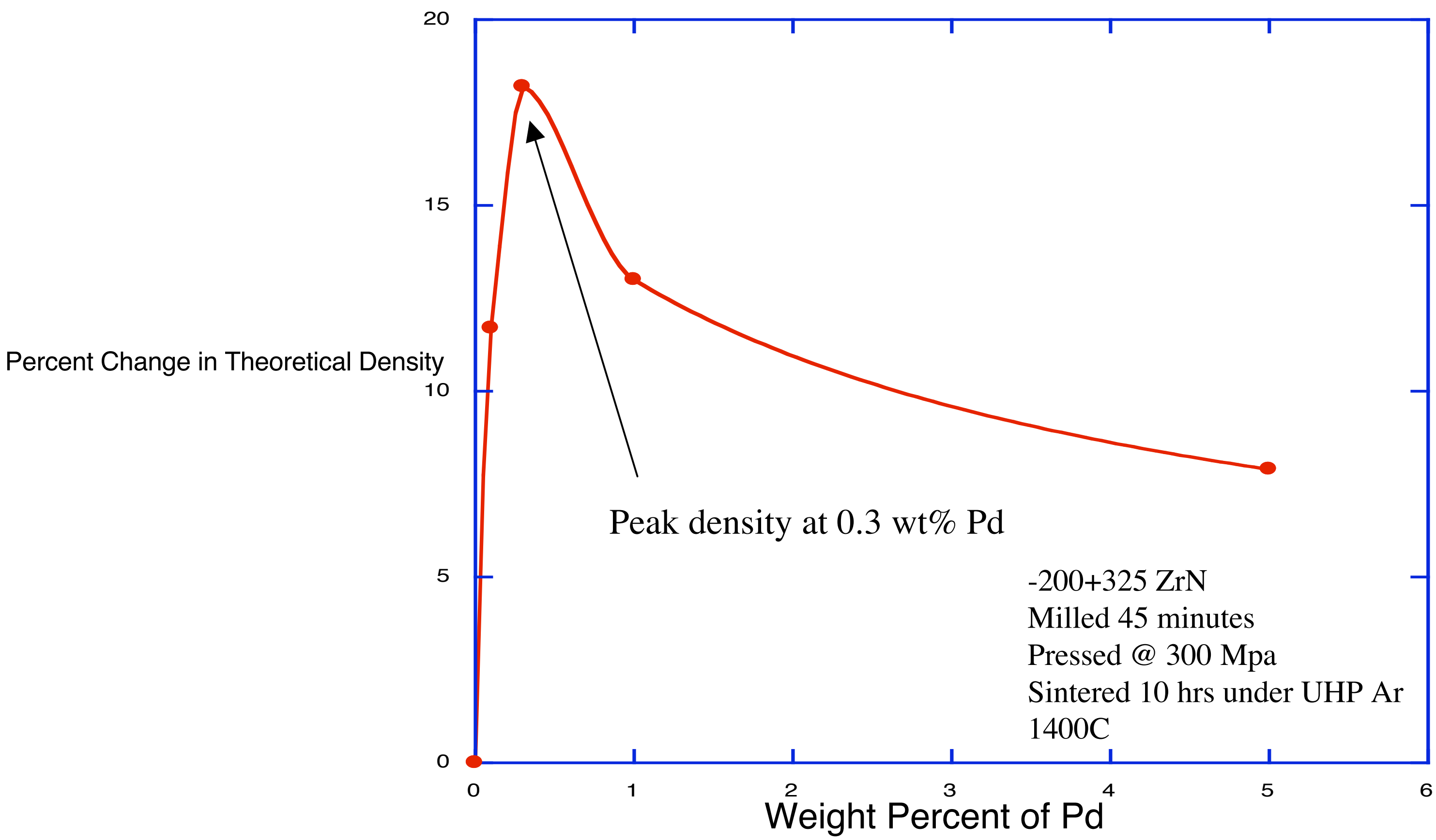
11-H 11-L 13 21-H 21-L 23

Sintering Aids

Sintering Aid	Increase in Density	Decrease in Density	No Change
Ni	✦		
Pd	✦		
Mn			✦
Sc			✦
Al		✦	
Si		✦	
Cu			✦

Sintering

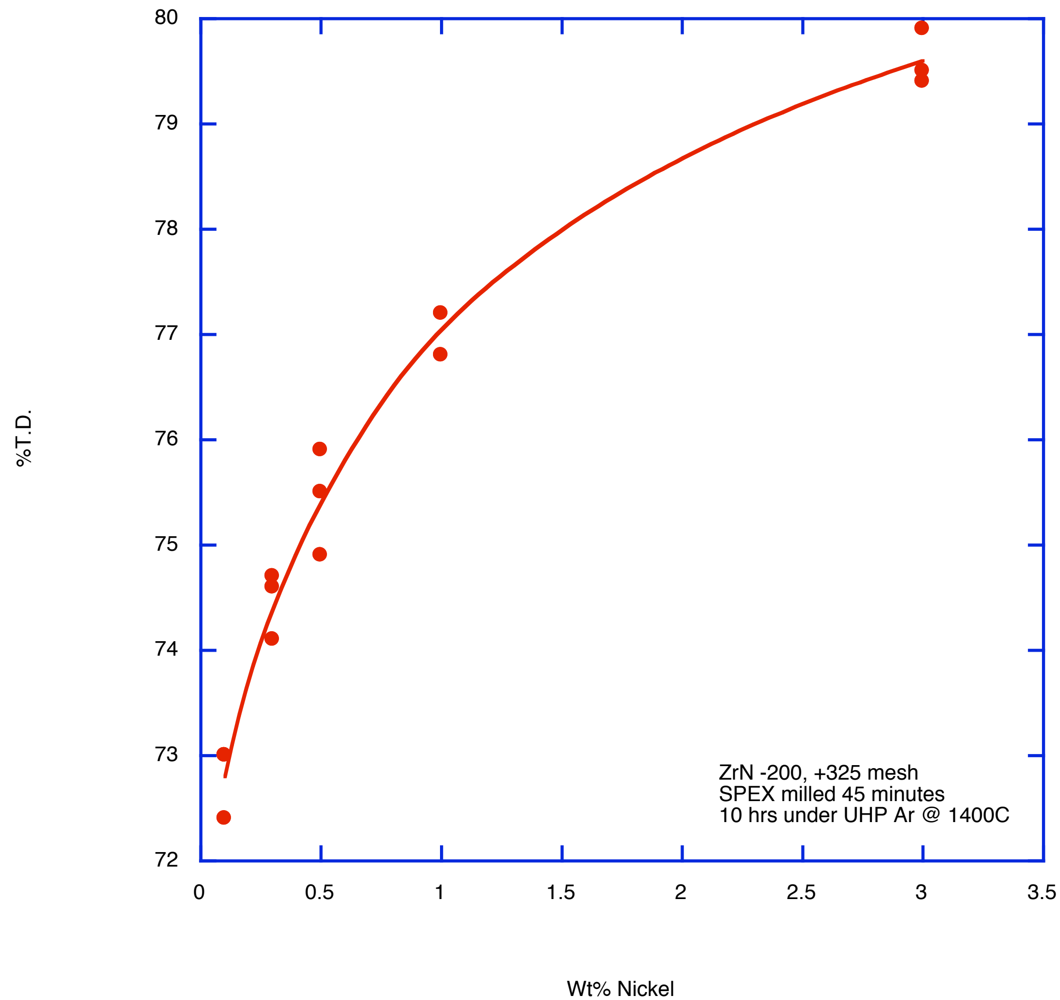
- Of all candidate sintering aids, Pd showed the most promise.



Pd additions are beneficial to pure ZrN

Sintering

- Ni also gave large increases in density



Phase Stability in Am-N System

Electronic Structure (ES) calculations of Am

Completed

Modified Embedded Atom Method (MEAM) model of Am.

Completed

ES calculations of Am-N

Completed

MEAM model of AmN.

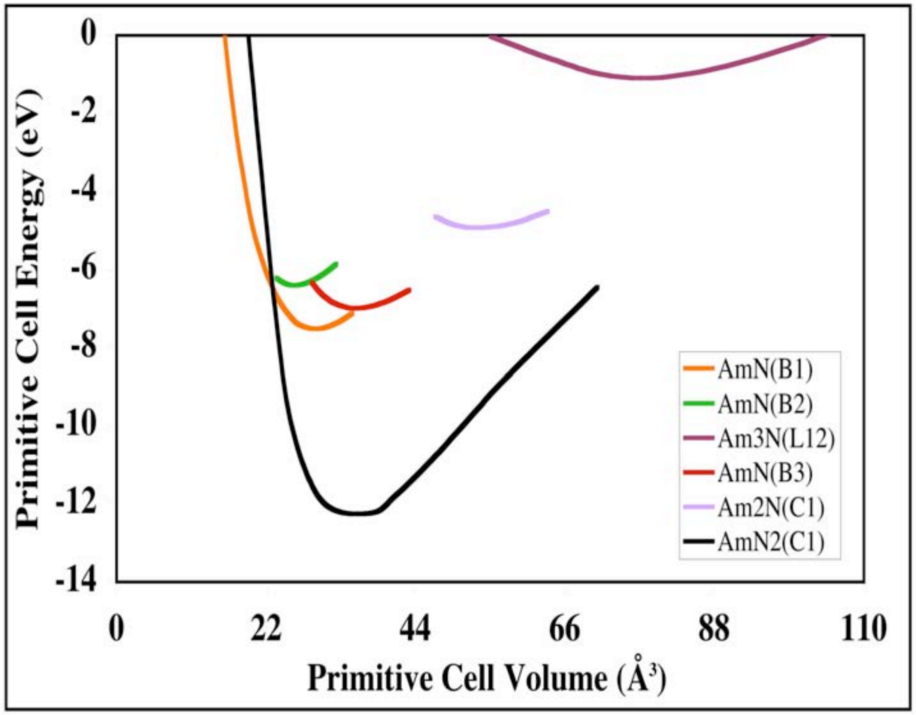
Completed

Free energy calculations of Am-N phases

In progress

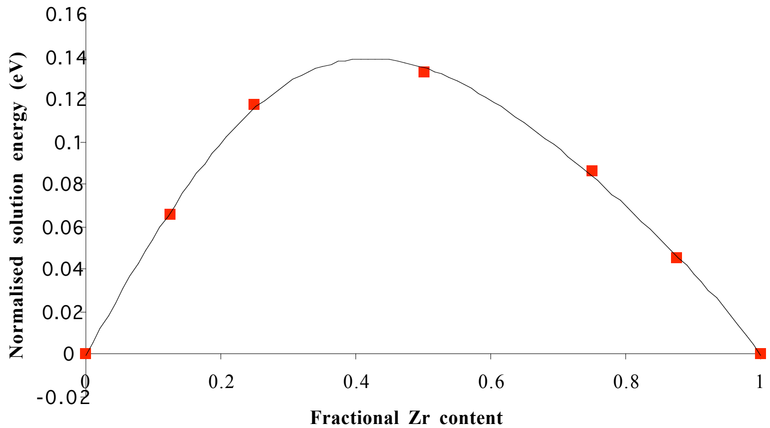
Am-N phase diagram

NOTE: There is NO Am-N phase diagram available at this time in the literature.

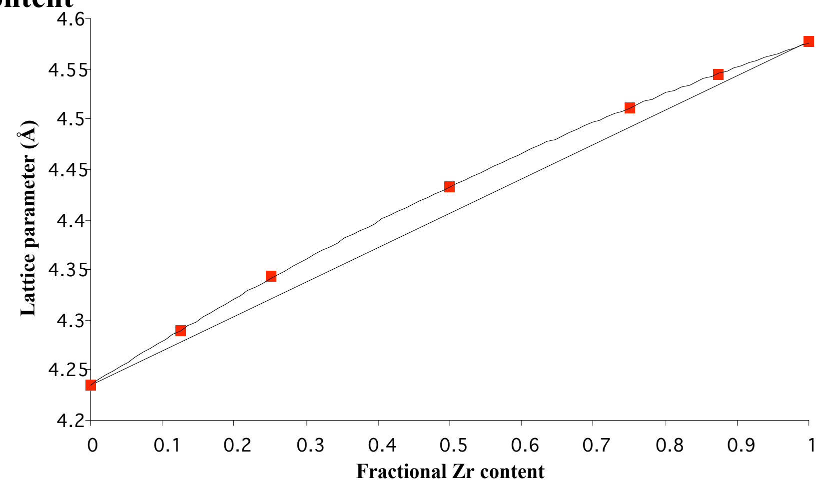


Energy versus volume for various AmN line compounds from electronic structure calculations.

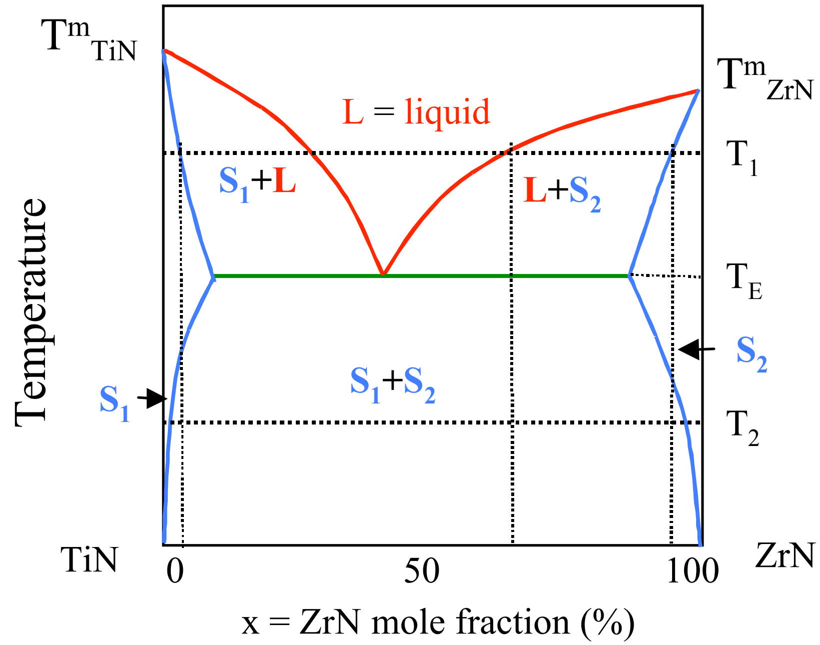
ZrN-TiN Phase Diagram from Quantum Mechanics Calculations



Solution energy (eV) as a function of fractional zirconium content



Lattice parameter of $Zr_xTi_{(1-x)}N$ as a function of x

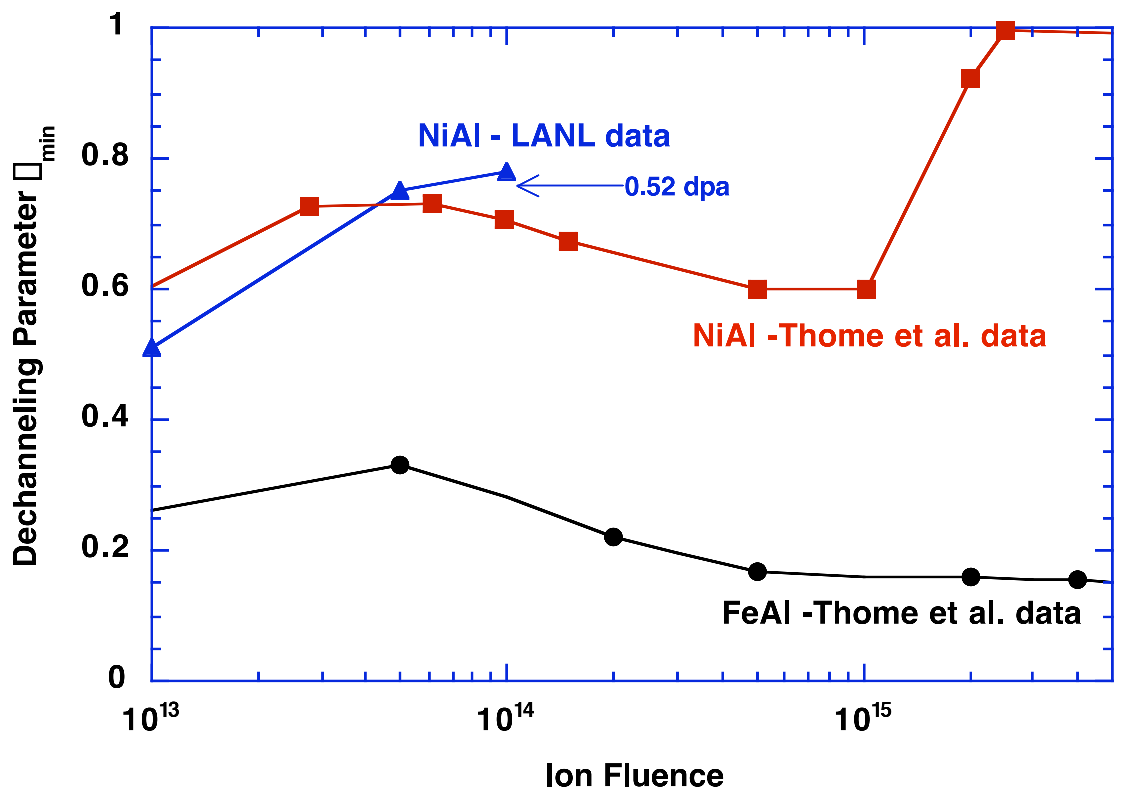


G ^{liquid} is based on a quasi ideal solution of ZrN and TiN liquids.

G ^{solid} is an estimate based on the quantum mechanical calculations and Bragg-Williams theory for a ramdomly mixed solid solution.

– The diagram is qualitative, both solution models require refinement

Ion Channeling Measurements of Damage Accumulation in Xe-ion Irradiated Single Crystal NiAl and FeAl



Preliminary measurements at LANL on NiAl show similar results to a previous French study. Additional work is necessary to determine whether the unusual behavior of damage recovery with increasing ion dose is observed.

L.Thome, C.Jaouen, J.P. Riviere and J.Delafond
Nuclear Instruments and Methods in Physics Research B19/20 (1987) 554-558

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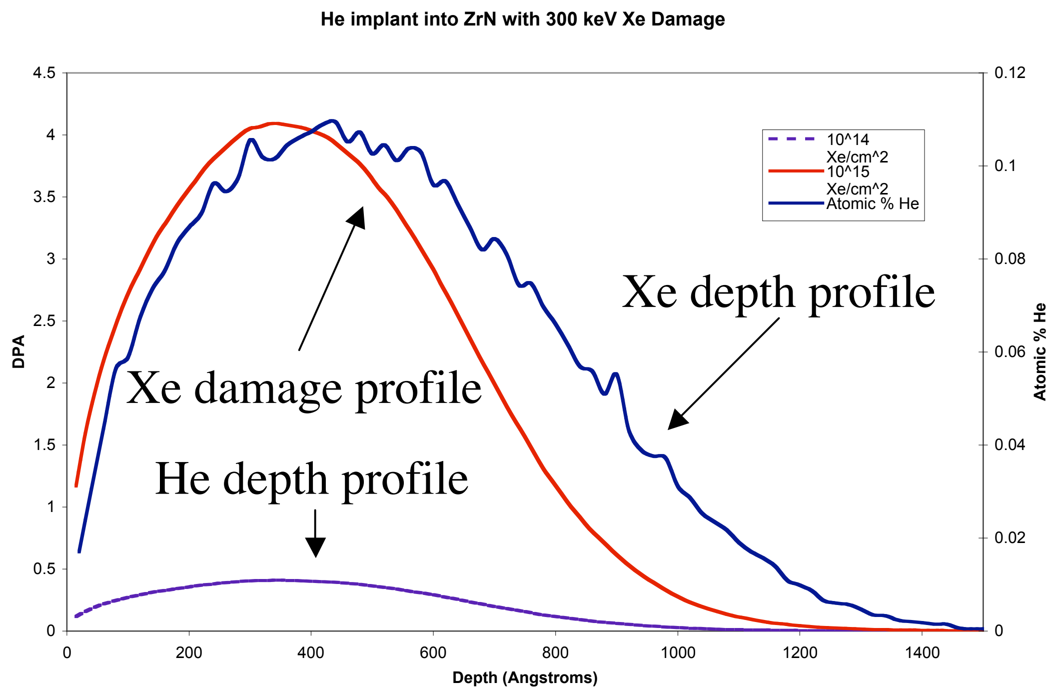
He Release with Xe Damage in ZrN

- Xe was implanted @ 300 keV at different amounts causing different displacement damage (dpa)
- He was implanted at 15 keV and 60° to place it at the same depth of the Xe damage
- Samples were heated in a vacuum furnace at 25°C/s
- He release was monitored by a residual gas mass spectrometer
- Implantation was done at LANL and He analysis at PNNL



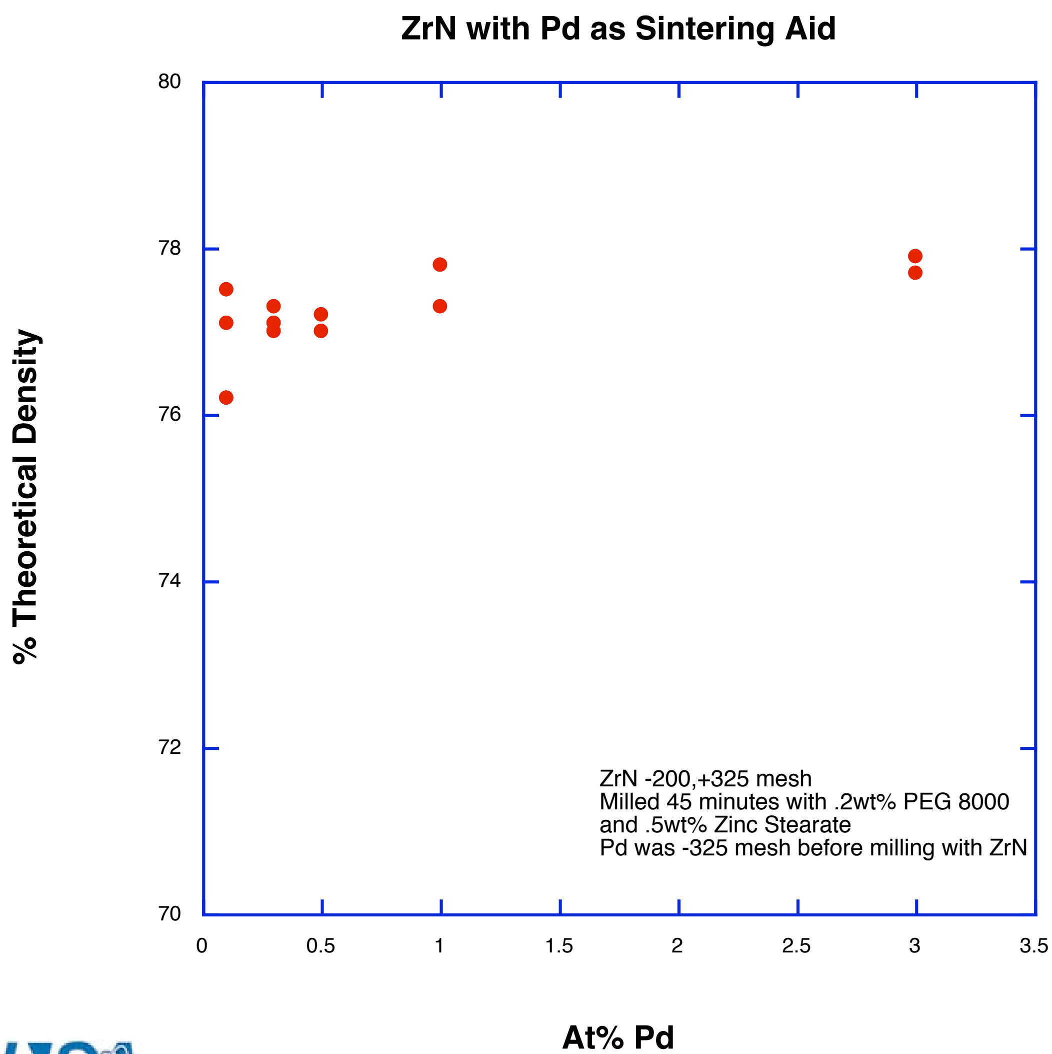
Summary

- AFC-1AE nitride pellets have been fabricated, characterized, and shipped to ANL-W
- Improved processing led to improved pellet intregrity
- Cold pellet development continues to support actinide nitride work
- He release from ZrN is complicated
- Thermal treatment of ZrN can influence mechanical properties
- NiAl appears to be radiation tolerant

Sintering

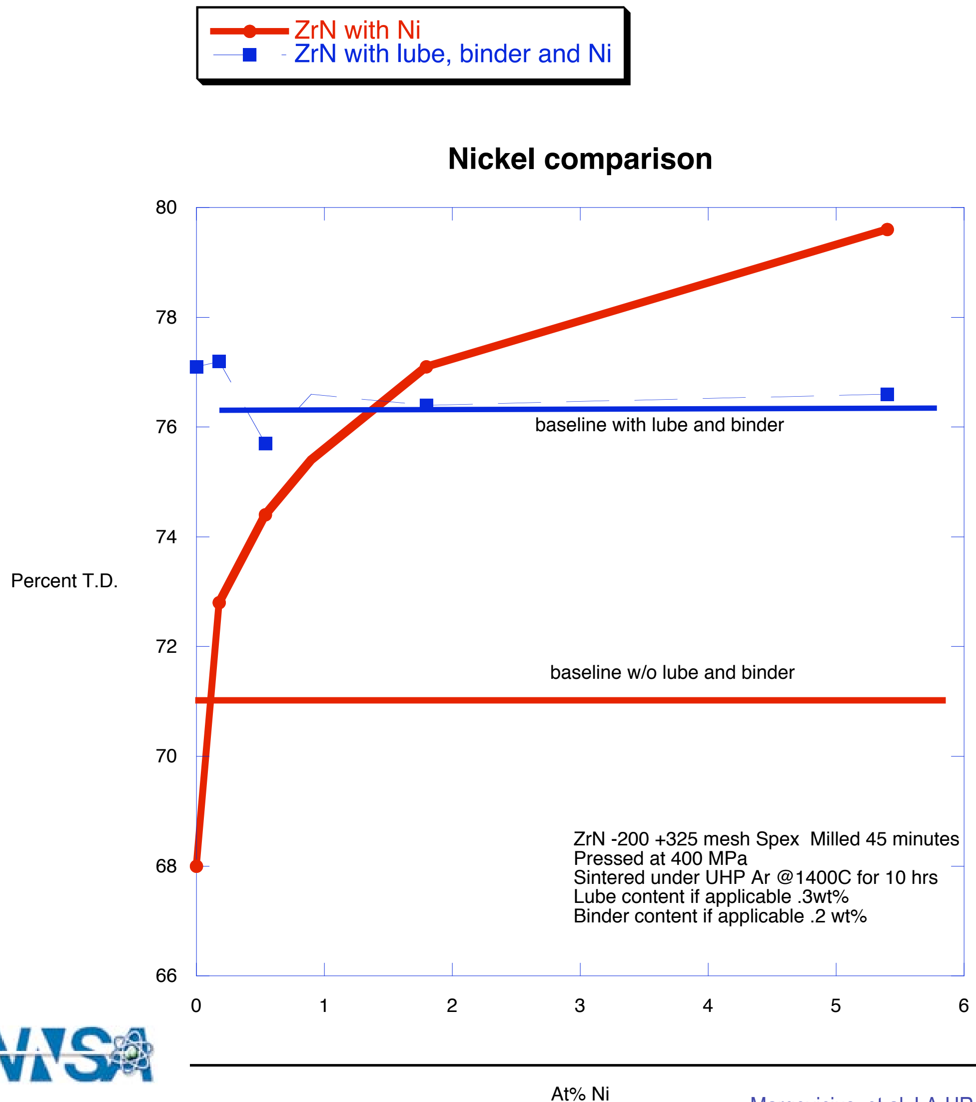
- Once Pd and Ni had been indentified as sintering aids, the optimized parameters were then used and Pd and Ni added in the same amounts and sintered once again.
- Pd nor Ni showed the same increases with the optimized powder process.

Pd Sintered with Optimized Powder



As can be see in the graph to the left, there is no increase observed. Based on previous data there should be a spike in density at .3 at%.

Ni Sintered with Optimized Powder

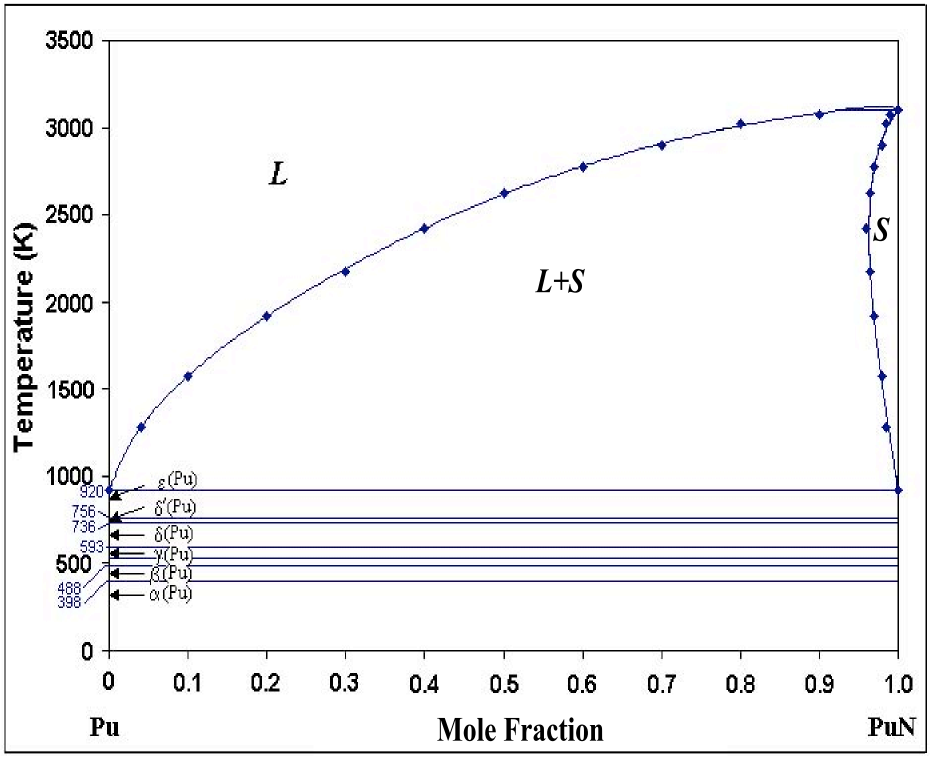


Here the same problem surfaces again. Although initial density with the optimized parameters is much higher, the pellets don't densify as much at higher temperatures or with previously proven sintering aids.

Phase Stability in Pu-N

A CALPHAD (Computer Coupling of Thermochemistry and Phase Diagrams) approach was used to retrieve the free energy of all phases in the Pu-N System. The model reproduces the currently available phase diagram[1].

The free energy will be further used for phase stability calculations in multi-component systems such as PuN-UN-AmN.

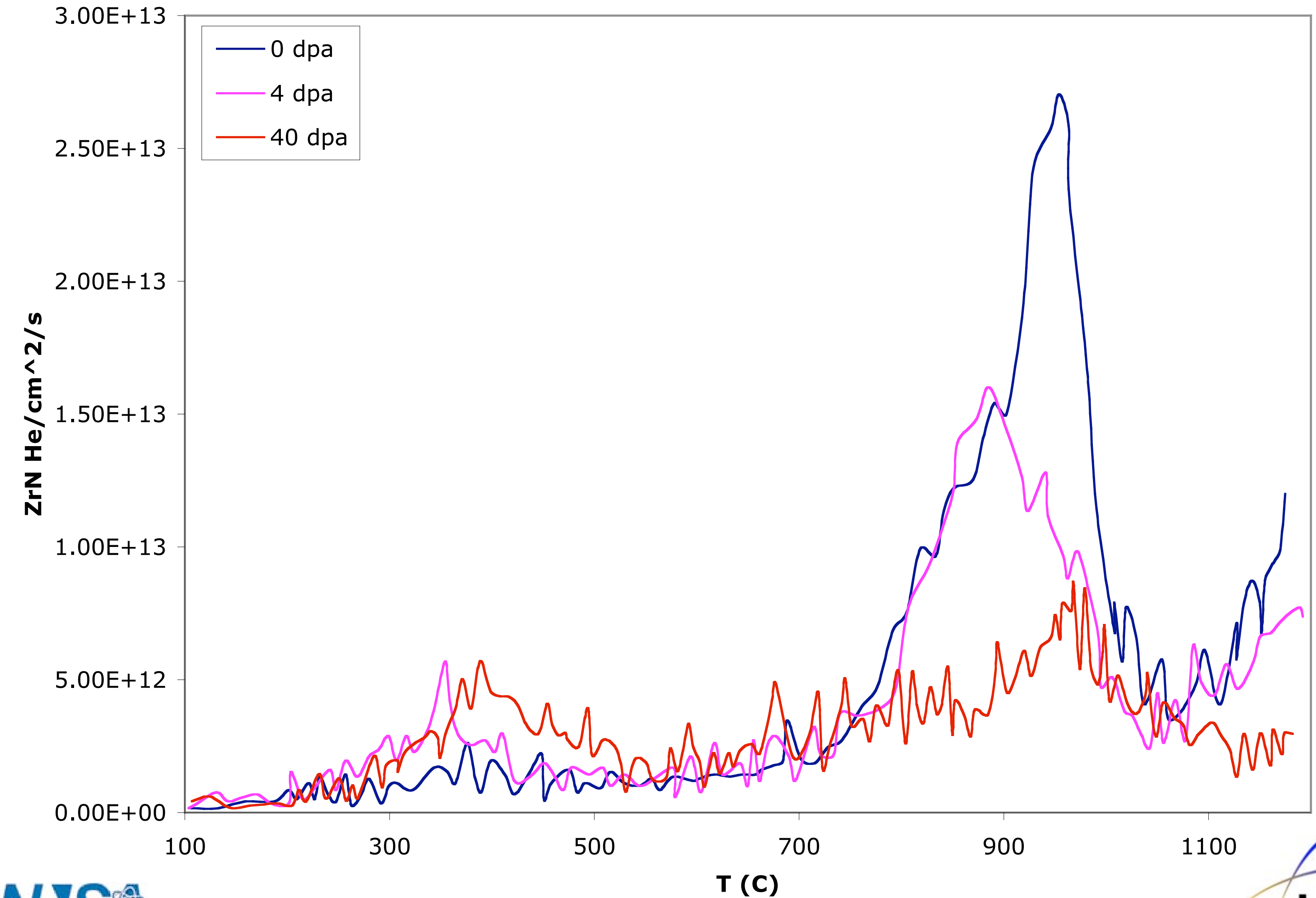


Assessment of the Pu-PuN Phase Diagram
and comparison with data (dots) reported by Wriedt[1]

*Los Alamos National Laboratory

[1]H. A. Wriedt, "The N-Pu Phase diagram" in "Phase Diagrams of Alloys", Editor T. B. Massalski, ASM International, 1970.

He Release From ZrN w/ Xe Damage



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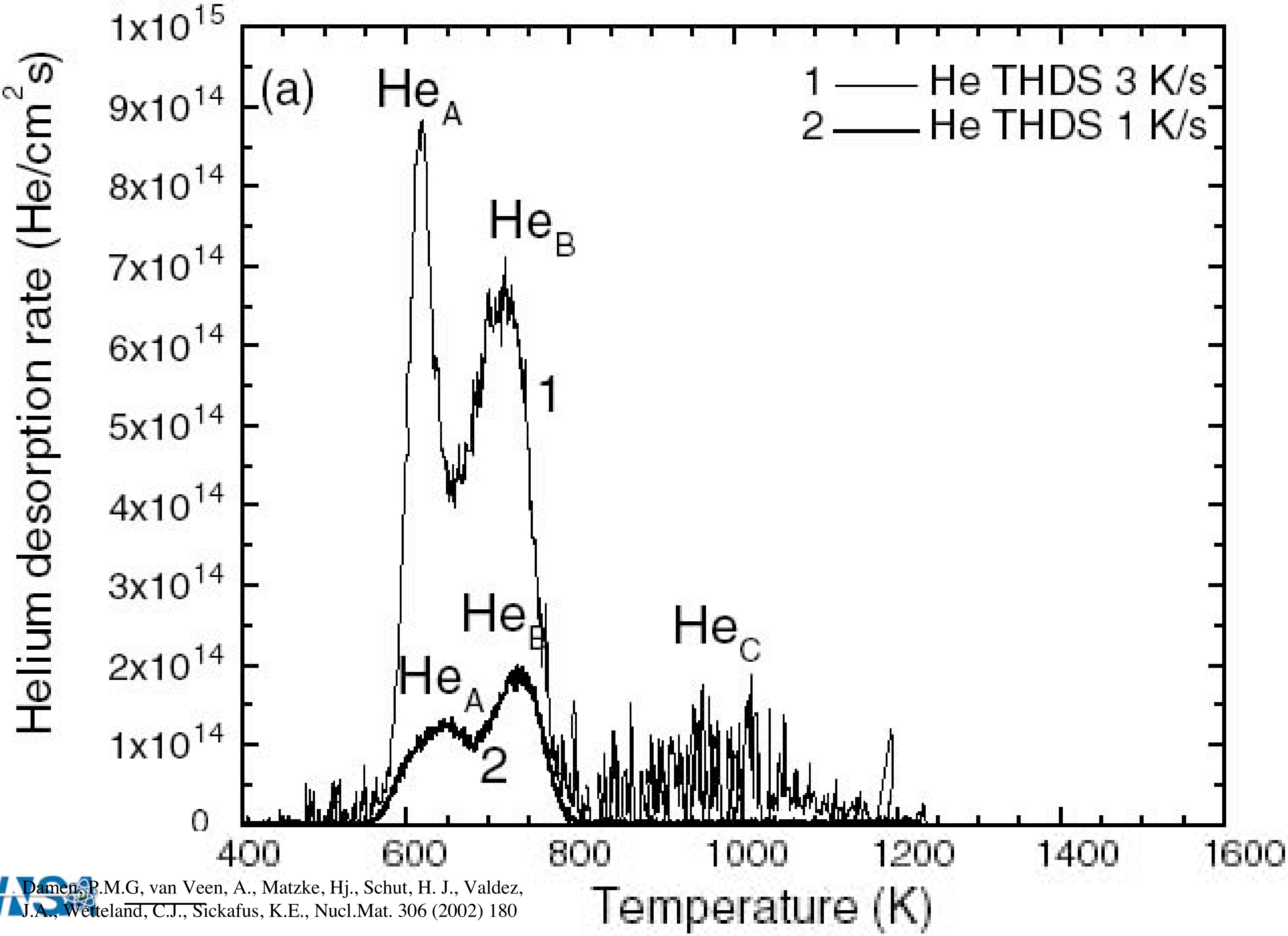
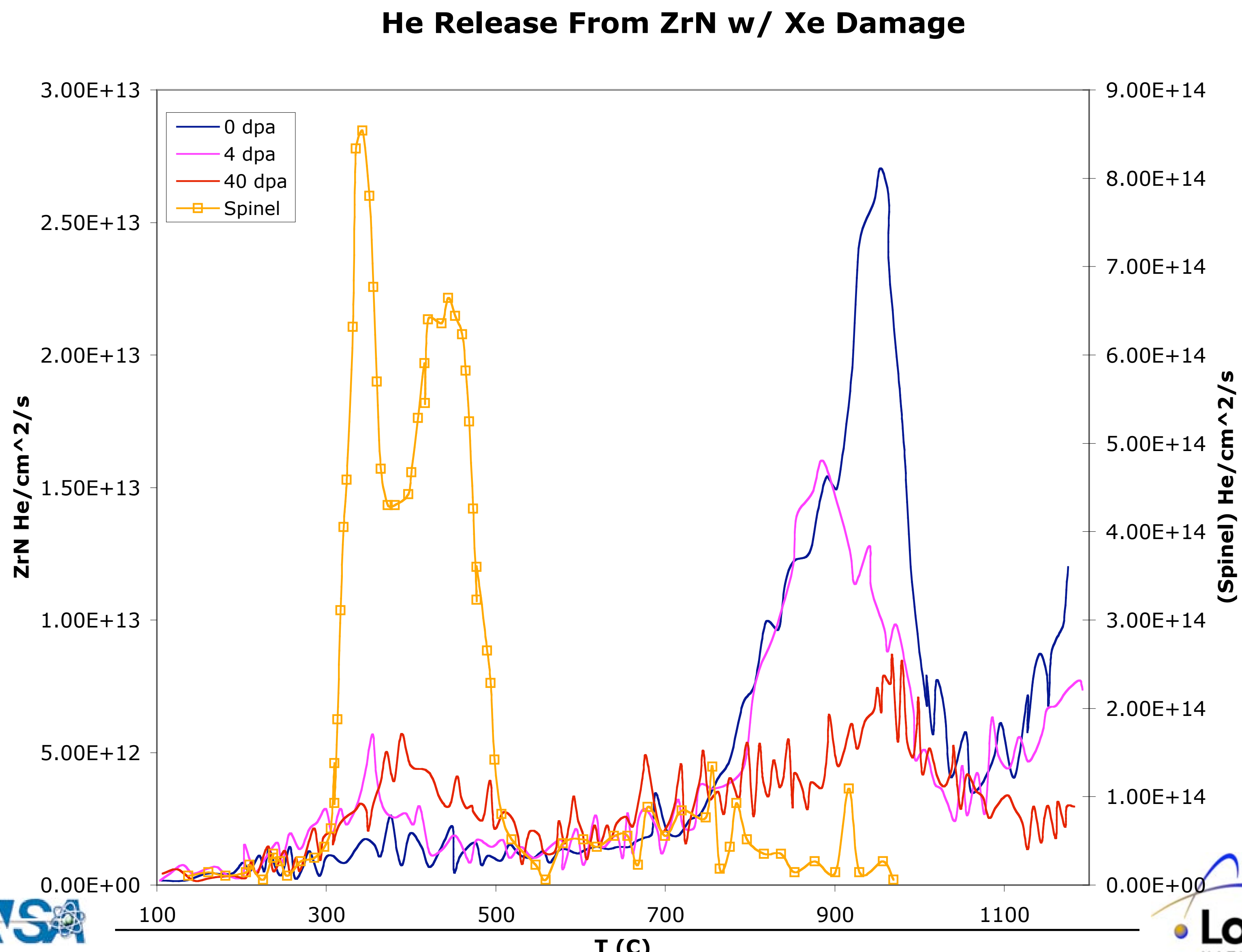
He Release from Spinel



Damen, P.M.G, van Veen, A., Matzke, Hj., Schut, H. J., Valdez, J.A., Wetteland, C.J., Sickafus, K.E., Nucl.Mat. 306 (2002) 180

He Release in ZrN Compared with Spinel



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He Release Results/Comparison

Undamaged ZrN releases He in two stages

- ~ 950 and 1150°C

With increasing Xe damage, He shows a small release at ~ 350°C

- 1E15 Xe/cm2 ~ 4 dpa
- 1E16 Xe/cm2 ~ 40 dpa

Large amount of He unaccounted for

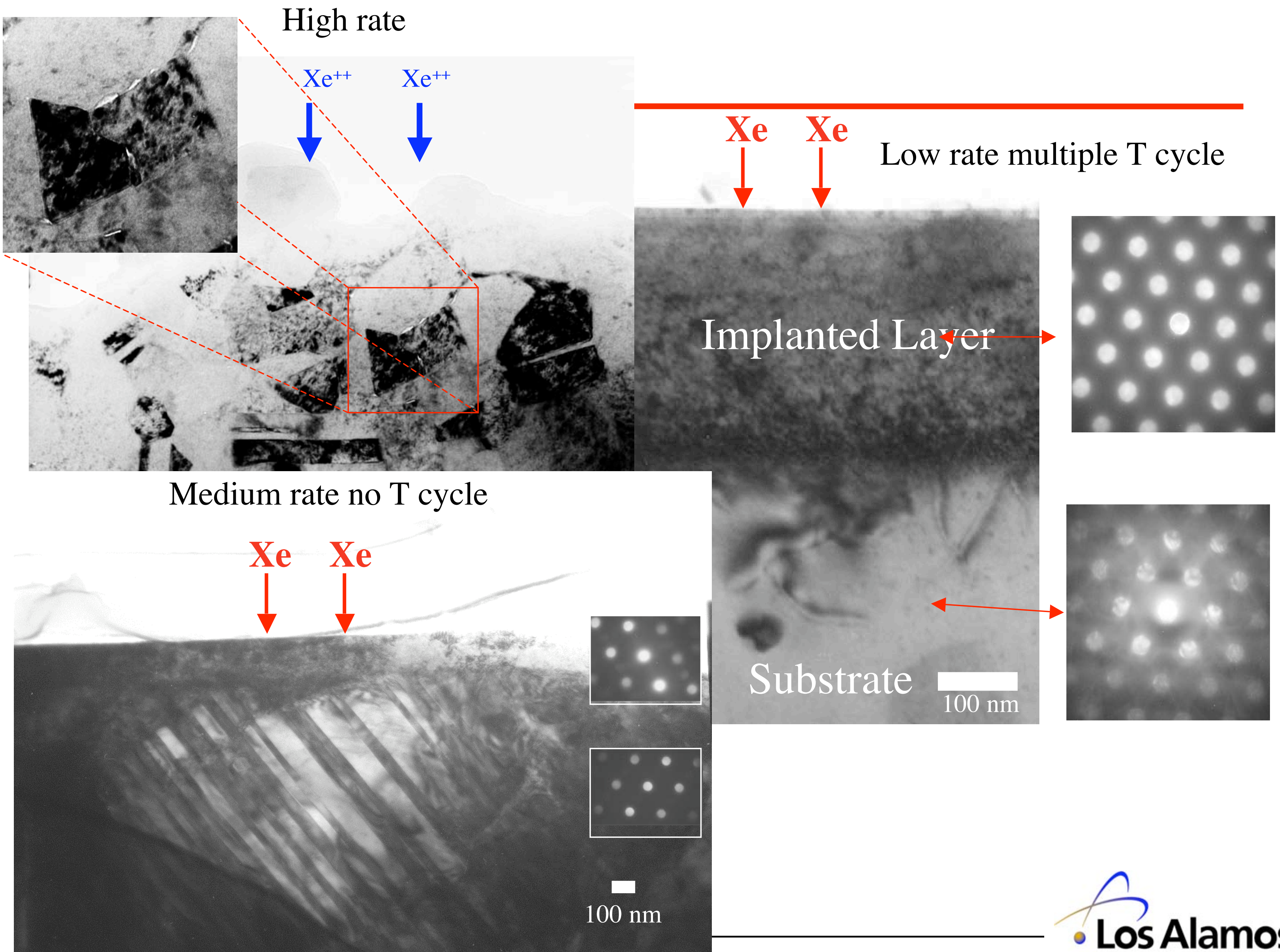
- Observing ~10% of implanted He that is reduced with damage
- Reduced to ~5% with 40 dpa
- Still trapped and requires higher temperature to evolve?

Amorphized spinel

- Study done at ITU by similar techniques
- Similar He and Xe irradiations, release in three stages
- Most pronounced at ~ 340 and 440°C, a third at 750°C
- Virtually all He released by 1000°C

Implantation/Thermal Cycle Effects

- ZrN has withstood Xe irradiation to very high fluence and damage
  - (>5E16 Xe/cm^2 and >200 dpa)
- By thermal cycling and/or reducing the implant rate the microstructural response observed has varied greatly
  - Grain refinement with microtwins and grain boundary bubbles at high rate 1 thermal cycle
  - Dense defects with dislocation shooting out of implanted region at very low rate or multiple thermal cycles
  - Medium rate with 1 thermal cycle produce the twins and defect band, but no grain refinement
    - Thermal cycles from ~ 300 to 100 back to 300 K
- No amorphization has yet been observed



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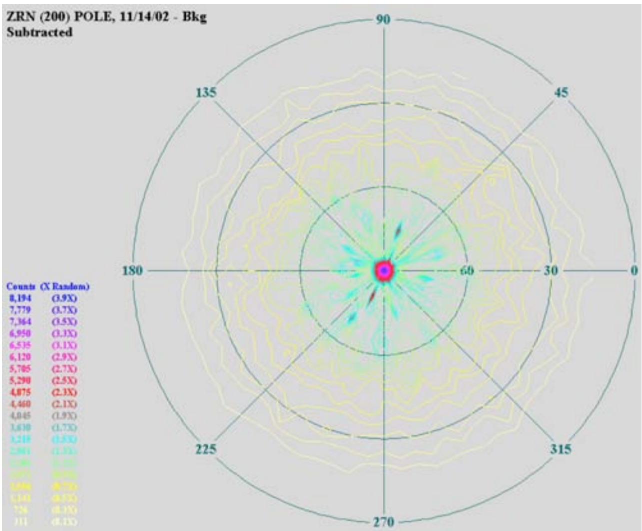
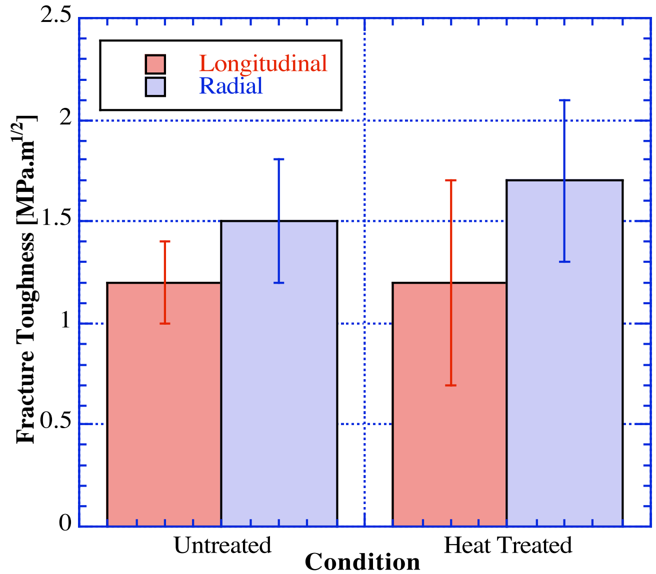
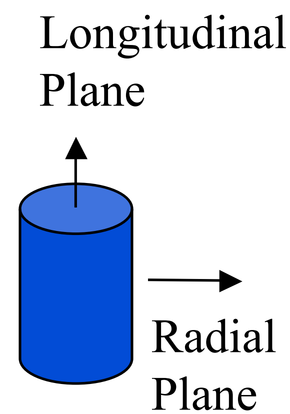
Texture and Mechanical Behavior Anisotropy

- A well-defined fiber texture is present in sintered pellets
- The texture leads to anisotropic behavior, particularly in the fracture toughness.
- Mechanical properties are also affected by heat treatment for different sample planes.



Uniform (200) fiber texture



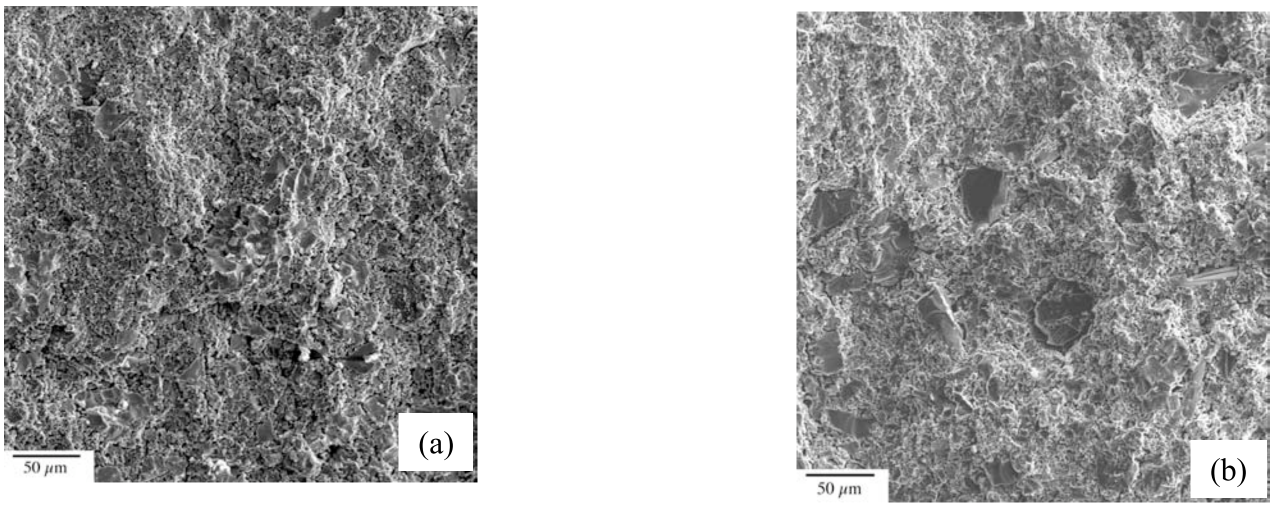


Fracture toughness as a function of heat treatment and fracture plane.

A proper combination of sintering, heat treatment and pellet orientation can be used to increase structural reliability

Heat Treatment and Microstructure

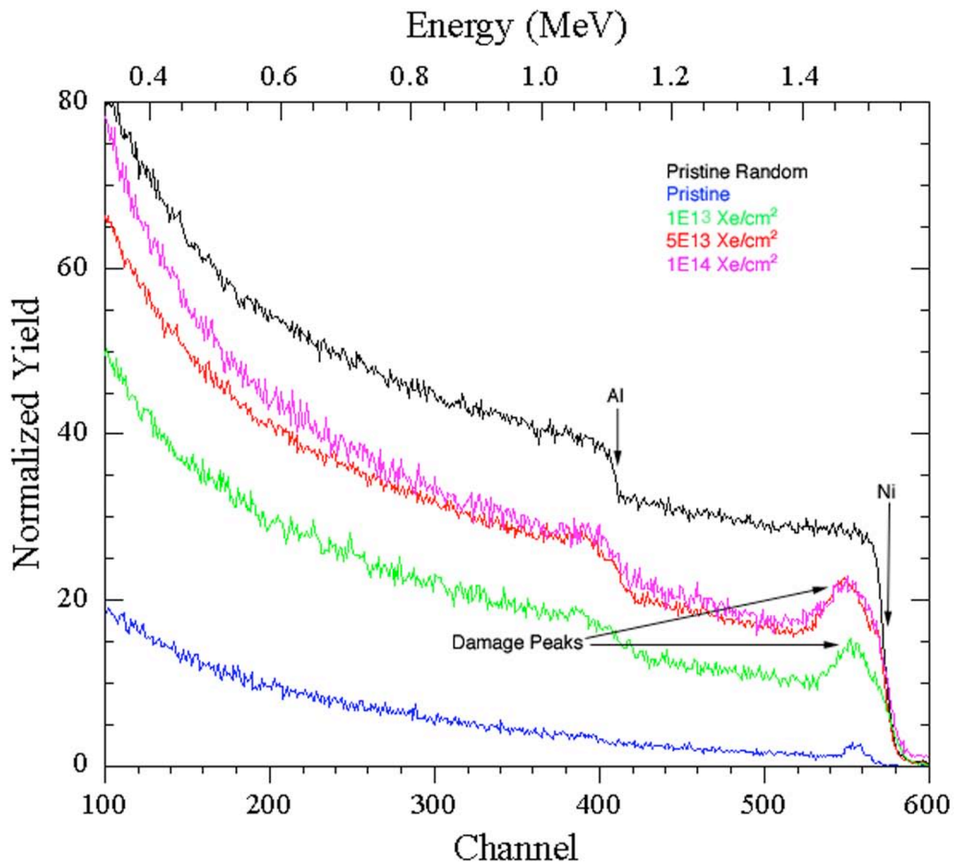
- Increase of fracture toughness was correlated to an increase in the fraction of cleaved particles after heat treatment
- Preliminary results using Electron Microprobe indicate higher nitrogen content as well as oxygen in treated specimens.
- Higher nitrogen and oxygen in treated samples increase interfacial strength.



Fracture surfaces on the radial plane for (a) untreated sample, (b) treated specimen

RBS of NiAl Single Crystal

Rutherford Backscattering and Channeling (RBS/C) spectra illustrating damage accumulation of single crystal NiAl irradiated with 450 keV Xe+++ ions.



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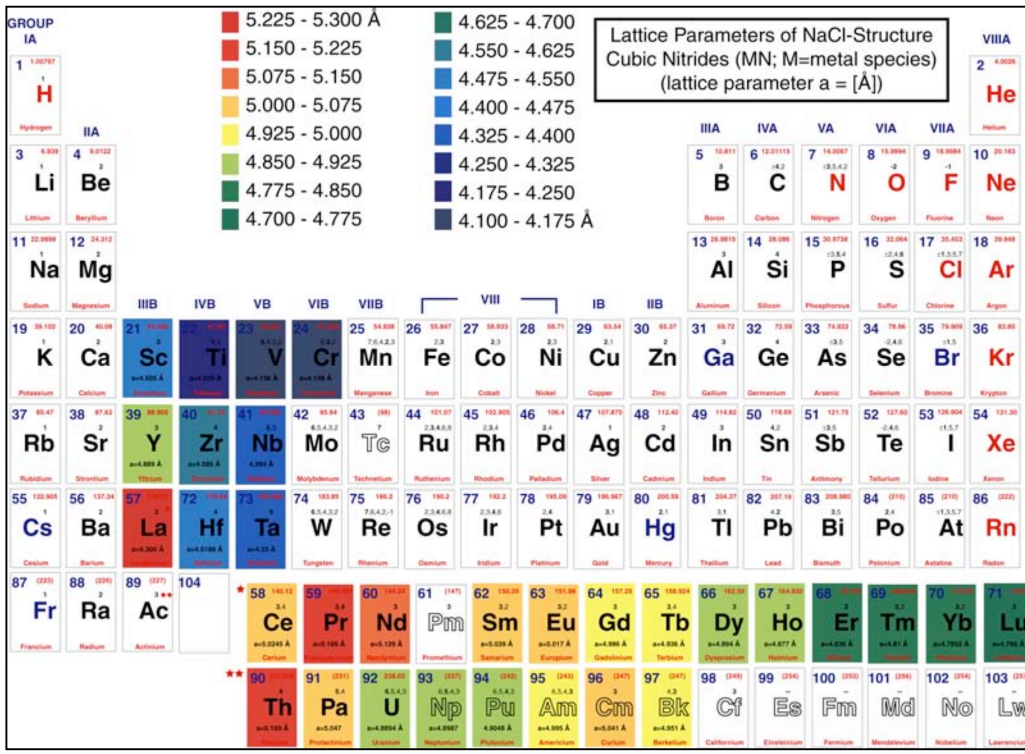
Nitrides show attractive properties

Fuel Type	Metal Density (g/cm^3)	Melting Point (K)	Thermal Conduct. (W/(m·K))	Relative Stability (thermal or phase)	Fission Gas Release
U	19.05	1408	25	Low	Low (swelling)
UO_2	9.65	3100	2.5	Moderate	High
UN	***13.52***	***3050***	***24***	***Moderate-high***	***High***
UC	12.97	2760	23	High	Moderate

All actinide nitrides have MN phases and are 100% soluble



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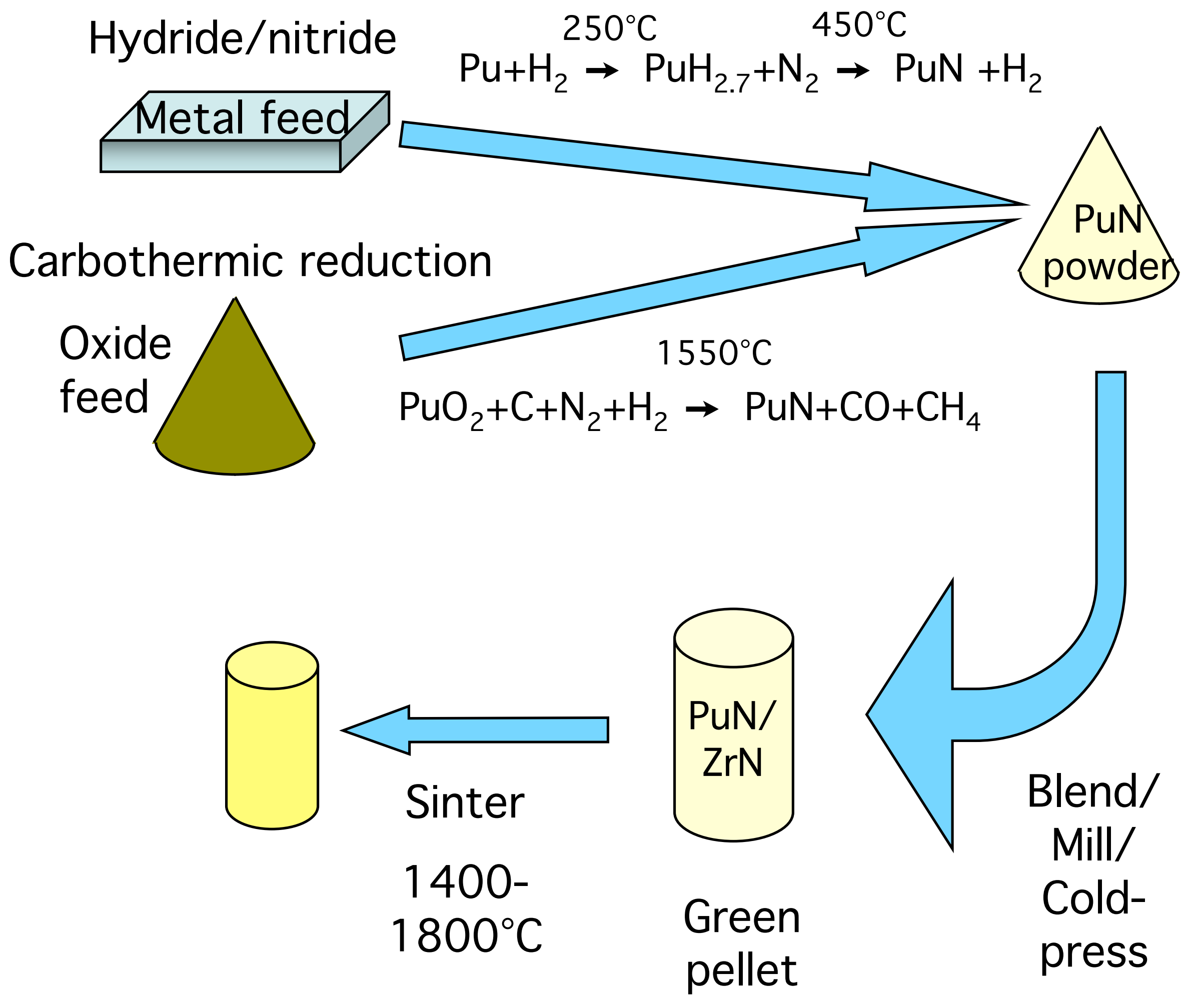
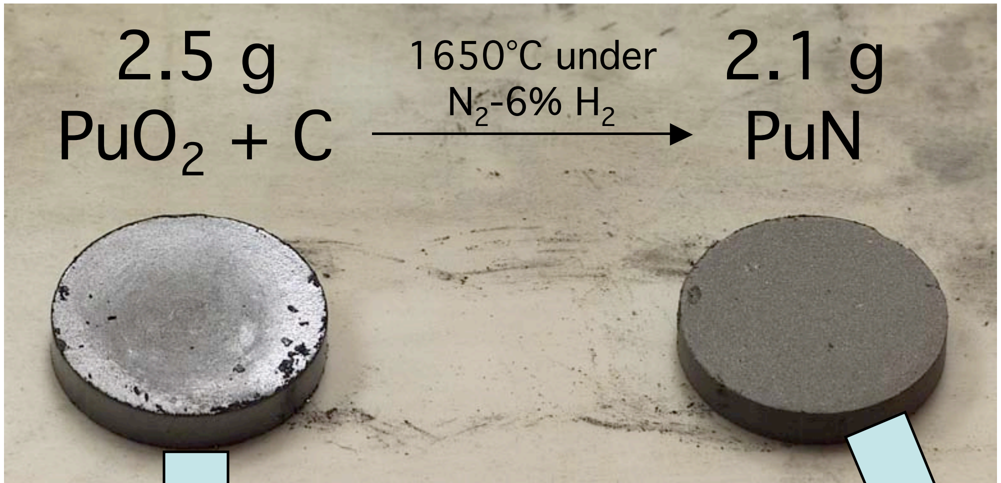
Nitride pellet synthesis



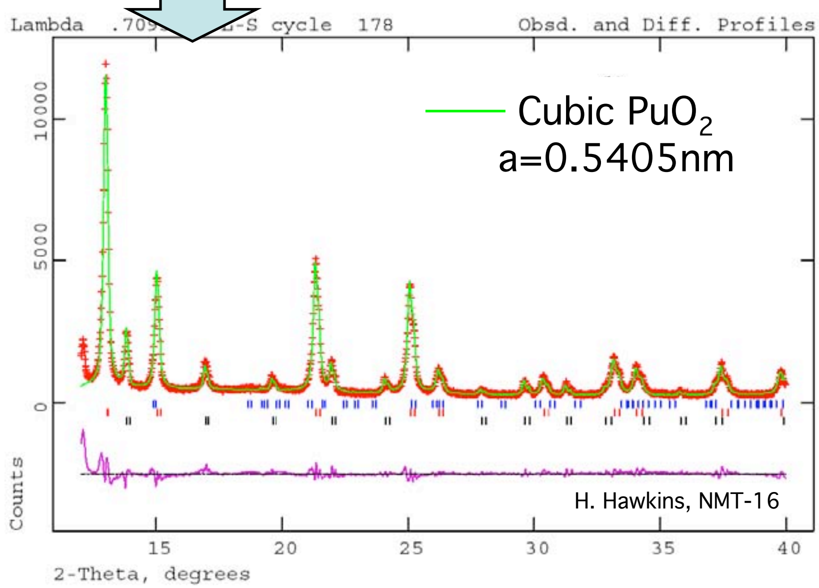
Carbothermic Reduction to Nitride

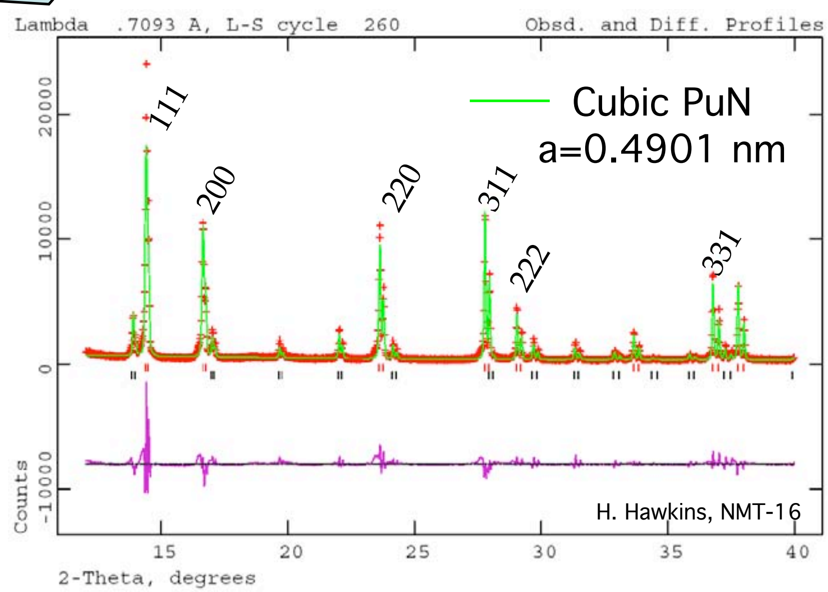


Oxide-to-nitride conversion:
predicted weight loss 16.0%
measured weight loss 16.2%

Appearance:
Silver/gray to gold

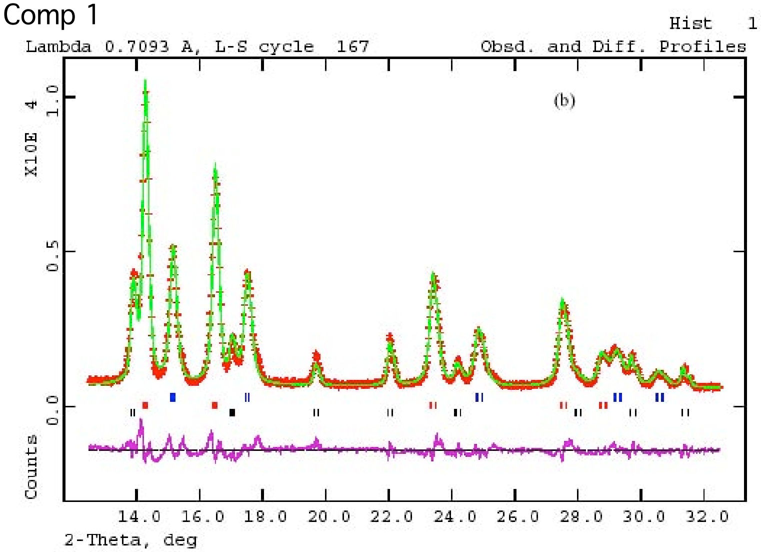
X-ray diffraction:
NaCl structure
predicted a: 4.905 angstroms
measured a: 4.901 angstroms





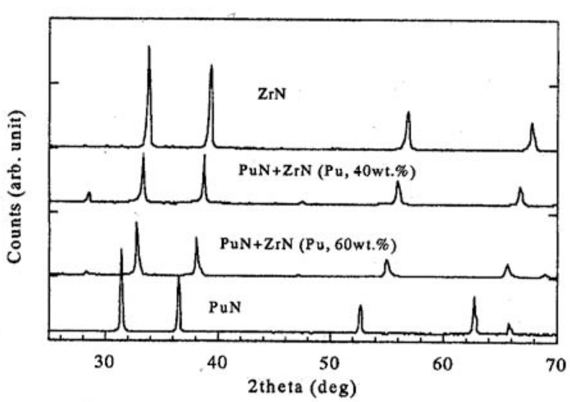
X-ray diffraction for ATR nitirdes

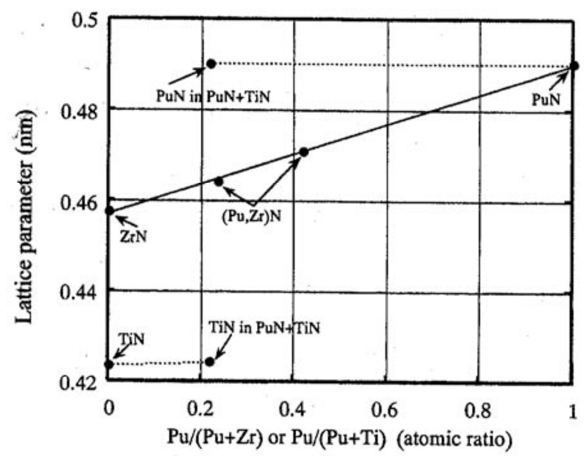
Comp 1



Before Sintering	ZrN 4.61 A	PuN 4.91 A

After Sintering	ZrN 4.61 A	(Pu-Zr)N 4.76 A	PuN 4.91 A





- *Only one crystal structure, rocksalt, was identified*
- *No free metal and little oxide observed*
- *Usually two rocksalt structures with differing lattice parameters was observed*
- *Suggests the incomplete interdiffusion of actinide nitride with zirconium nitride*

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Non-fertile: optical ceramography